Statistical Mechanics
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Lecture - 07
Free Energy in Thermodynamics

So, this is one of the negative of the Hamiltonian does not matter, but this is related to the Hamiltonian of the system.

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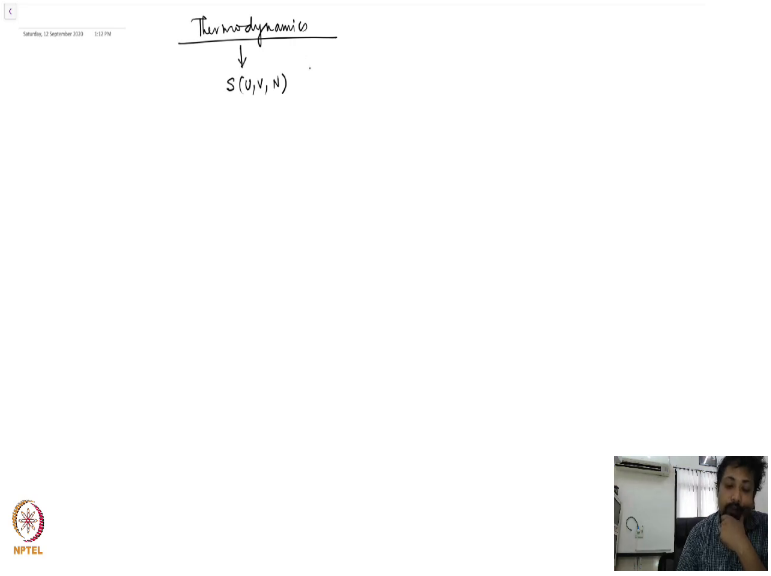

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Thermodynamics

$\downarrow$

$S(U,V,N)$

So now, what about in thermodynamics?

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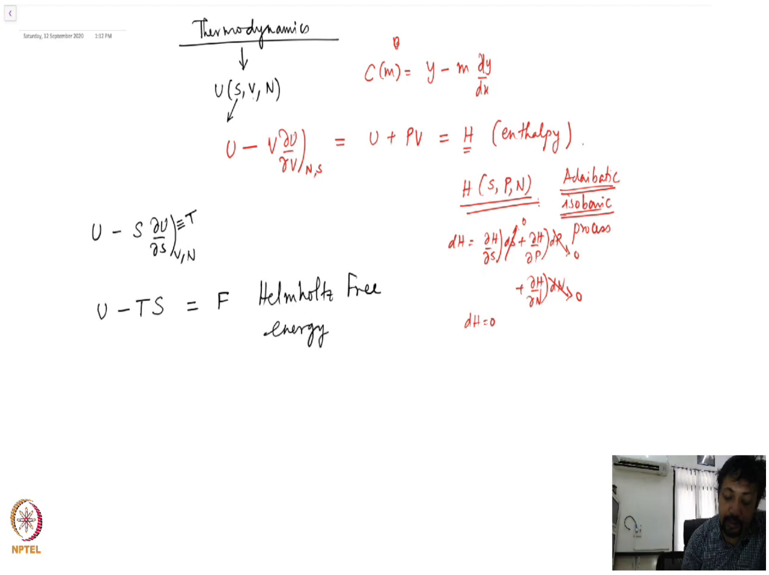

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Thermodynamics

$\downarrow$

$U(S, V, N)$

$C(m) = y - m\frac{dy}{dx}$

$U - V\frac{\partial U}{\partial V}\Big)_{N,S} = U + PV = \underline{\underline{H}}$ (enthalpy).

$\underline{\underline{H(S, P, N)}}$ Adaibatic isobaric process

$dH = \frac{\partial H}{\partial S}\Big)\overset{0}{\cancel{dS}} + \frac{\partial H}{\partial P}\Big)\cancel{dP}\rightarrow 0$

$+ \frac{\partial H}{\partial N}\Big)\cancel{dN}\rightarrow 0$

$dH = 0$

$U - S\frac{\partial U}{\partial S}\Big)_{V,N} \equiv T$

$U - TS = F$ Helmholtz Free energy

I have S as a function of U, V, N, correct or since I am talking about we will be talking about free energies we will start with U as a function of S, V, N. I want to replace that volume, correct. If I want to replace the volume then I have the prescription that is given to me that I need to define a new function which is y minus m times dy dx.

Here it is a function of a single variable I can generalize this; therefore, I will define a function which is U minus V del U del V and N and S also this is allow, correct. What is this function? But, this is U and del U del V is PV and this I know is the enthalpy H. So, I have defined a new thermodynamic potential where essentially is a I have defined a new thermodynamic potential where I place the volume by its conjugate force P.

And, clearly you can see that H is a function of S, P and N. So, that means, for an adiabatic isobaric process the enthalpy remains a constant quantity because there is no variation. So, if you look out dH, dH is going to be del H del S dS plus del H del P dP plus del H del N dN and since I have said that it is an adiabatic process it is an isobaric process this is 0, this is 0 and this is always 0 because I have I always take N to be fixed.

Therefore, dH is 0 and that essentially means that there is no change in the enthalpy. I can replace S. So, let me write down S del U del S V and N constant. This is U minus T S because I know that this derivative is equivalent to T if and this quantity is known as Helmholtz free energy.

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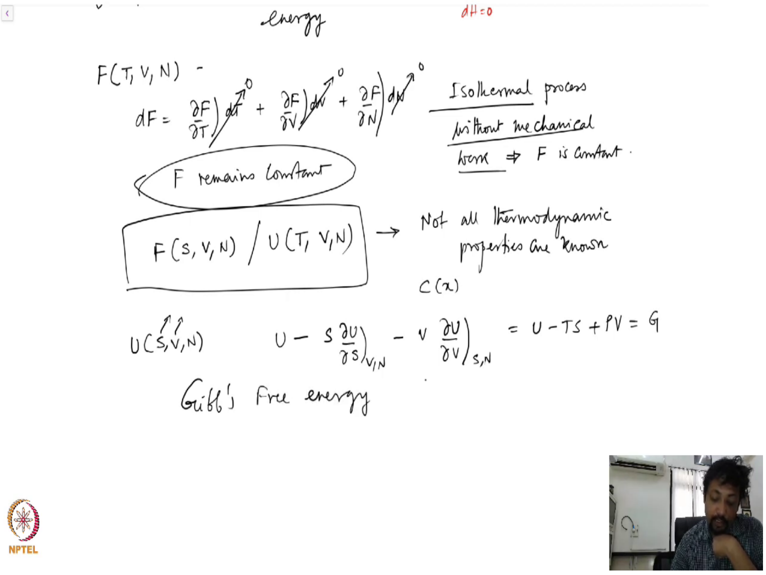

energy

$dH=0$

$F(T, V, N)$ -

$$dF = \frac{\partial F}{\partial T}\Big) \cancel{dT}^{0} + \frac{\partial F}{\partial V}\Big) \cancel{dV}^{0} + \frac{\partial F}{\partial N}\Big) \cancel{dN}^{0}$$

Isothermal process without mechanical work $\Rightarrow$ F is constant.

F remains constant

$$\boxed{F(S, V, N) \,/\, U(T, V, N)} \rightarrow$$ Not all thermodynamic properties are known

$C(x)$

$$U(S, V, N) \qquad U - S\frac{\partial U}{\partial S}\Big)_{V,N} - V\frac{\partial U}{\partial V}\Big)_{S,N} = U - TS + PV = G$$

Gibb's Free energy

Since I have replaced S and I have brought it brought in T the Helmholtz free energy is a function of T, V, N and clearly this means that dF is del F del T dT plus del F del V, dV plus del F del N dN. Isothermal process without mechanical work implies F is constant. So, isothermal means dT 0, mechanical work is 0; well, this is always taken to be 0 because there is a fix it is a fixed system with a fixed it is not an open system.

So, here therefore, F remains constant. So, you use the Helmholtz free energy whenever you have an isothermal process without any mechanical work. There is no volume expansion or so, and in which case in which case the free energy remains the same. I have now, before I do the next step one thing I want to emphasize that you see if you might ask that if I want to calculate I want to express F as a function of S, V, N or I want to look at U as a function of T, V, N.

If you work it out this way, then you will see that not all thermodynamic properties are known. So, this is like specifying c as a function of x that we had discussed earlier. Now, coming back to this I have U as a function of S, V, N. I have been replacing one variable one generalized coordinate.

I want to replace two let us replace S and V; that means, I want to construct something which is del U del S, V and N constant minus V del U del V, S and N constant. This I can easily do U minus TS plus PV right and in thermodynamics this is what is called the Gibbs free energy.

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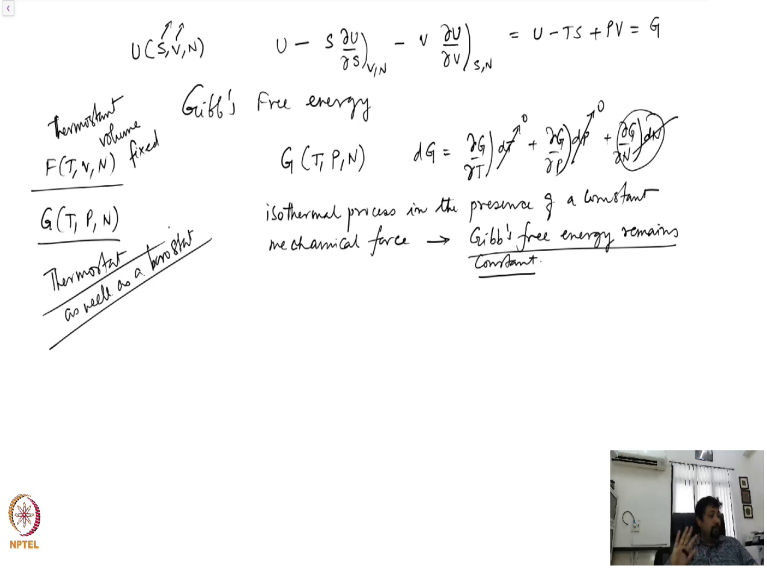

$U(\overset{\nearrow}{S}, \overset{\nearrow}{V}, N)$ $\quad U - S\left.\frac{\partial U}{\partial S}\right)_{V,N} - V\left.\frac{\partial U}{\partial V}\right)_{S,N} = U - TS + PV = G$

Thermostat volume fixed

$F(T, V, N)$

Gibb's Free energy

$G(T, P, N)$ $\quad dG = \left.\frac{\partial G}{\partial T}\right)\cancelto{0}{dT} + \left.\frac{\partial G}{\partial P}\right)\cancelto{0}{dP} + \cancel{\left.\frac{\partial G}{\partial N}\right)dN}$

$G(T, P, N)$

Thermostat as well as a barostat

isothermal process in the presence of a constant mechanical force → Gibb's free energy remains constant.

So, now, you must be utterly confused that why have I introduced another Gibbs free energy. You have to look at the Gibbs free energy very carefully T, V and N. Now, dG sorry I have replaced V with P dG is del G del T dT plus del G del P dP. I am holding N constant, but never mind. So, del G del N dN right.

In the presence of a constant thermodynamic a constant mechanical force, isothermal process in the presence of a constant mechanical force Gibbs free energy remains constant. So, isothermal process constant mechanical force this term is we always ignore because it is a closed system. Therefore, there is no particle exchange that is allowed. So, therefore, the Gibbs free energy remains constants.

So, there are two free energies one is F as a function of T, V, N; the other one is a function of T, P, N. They have different uses for different realizations. In this case you have a thermostat and volume fixed, and in this case you have a thermostat as well as a barostat, right. So, in that case the Gibbs free energy becomes the dominant becomes remains constant throughout the process.

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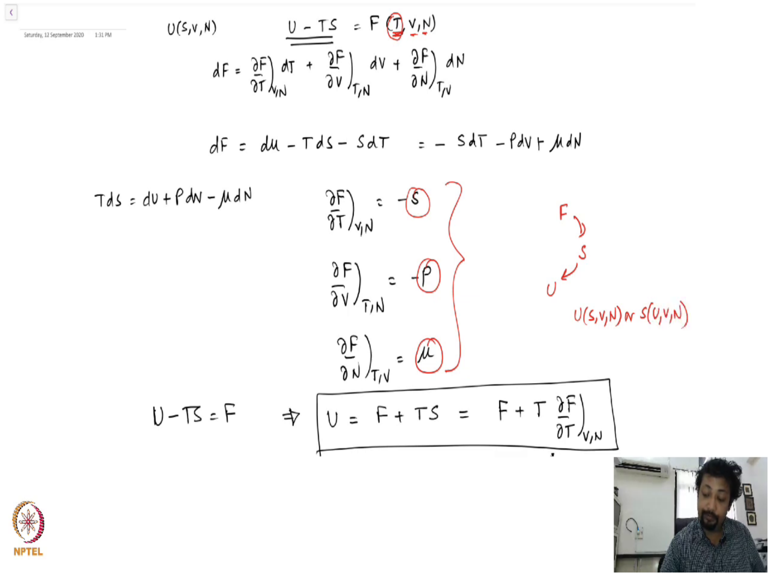

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$U(S,V,N)$

$$\underline{\underline{U - TS}} = F(T, V, N)$$

$$dF = \left.\frac{\partial F}{\partial T}\right)_{V,N} dT + \left.\frac{\partial F}{\partial V}\right)_{T,N} dV + \left.\frac{\partial F}{\partial N}\right)_{T,V} dN$$

$$dF = dU - TdS - SdT = -SdT - PdV + \mu dN$$

$$TdS = dU + PdV - \mu dN$$

$$\left.\frac{\partial F}{\partial T}\right)_{V,N} = -S$$

$$\left.\frac{\partial F}{\partial V}\right)_{T,N} = -P$$

$$\left.\frac{\partial F}{\partial N}\right)_{T,V} = \mu$$

F

S

U

$U(S,V,N)$ or $S(U,V,N)$

$$U - TS = F \Rightarrow \boxed{U = F + TS = F + T\left.\frac{\partial F}{\partial T}\right)_{V,N}}$$

So, now, we have seen how to use legendary transformation and we start off with this, and slowly can eliminate the generalized coordinates. So, if we eliminate entropy then we define this as not an equal to, but we define it as U minus T S which is my Helmholtz free energy function which is T, V, N. And, since it is a function of T, V, N, I can write down this as del F del T, V and N constant dT plus del F del V T and N constant dV plus del F del N T, N, V constant dN.

If you look at the left hand side dF is also identically dU minus T dS minus S dT and if you recall your first law T dS is equal to dU plus P dV minus mu dN. So, this means dU minus T dS is that is minus p dV plus mu dN. So, you immediately see if you compare that del F del T, V and N constant is minus S. del F del V T and N constant is minus P del F del N T and V constant is the chemical potential mu.

So, these three quantities can actually help you to determine the entropy the pressure and the chemical potentials these three relations sorry. So, once you know the once the Helmholtz free energy is given to you, you can calculate the; you can calculate this entropy from this relation and if you know the entropy please note that you can calculate U minus TS is equal to F which implies the internal energy is equal to F plus TS.

I can manipulate this expression and let us just do it very quickly. It is a very simple exercise. So, this is del F del T. Let us be very very careful here plus T del F del T volume and N constant, right. So, this I can write down del del T of F times T, am I right? So, if I do that then this the first term is F and the second term is T del F del T volume and N constant.

So, volume and particle number constant is implied over here. But, one can just calculate the internal energy as a function of U and once you know the internal energy as a function of U you know the entropy you can eliminate that forces to reconstruct that U as a function of S, V, N. So, these are the always the trick that you play.

So, you know F from this you calculate S, from this you calculate U and then you also know P and mu, the generalized forces that is given to you and F is always going to be a function of what? It is going to be a function of T, V and N. So, you see from these relations you can eliminate T and you can reconstruct back the fundamental relations U as a function of S, V, N or S as a function of U, V, N. We will do it as an exercise at the later stage.

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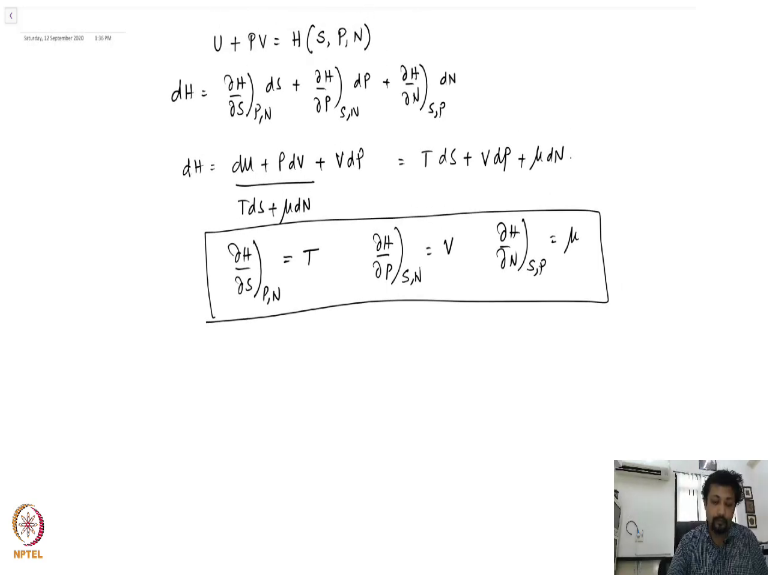

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$$U + PV = H(S, P, N)$$

$$dH = \left.\frac{\partial H}{\partial S}\right)_{P,N} dS + \left.\frac{\partial H}{\partial P}\right)_{S,N} dP + \left.\frac{\partial H}{\partial N}\right)_{S,P} dN$$

$$dH = \underbrace{dU + PdV}_{TdS + \mu dN} + VdP = TdS + VdP + \mu dN.$$

$$\boxed{\left.\frac{\partial H}{\partial S}\right)_{P,N} = T \qquad \left.\frac{\partial H}{\partial P}\right)_{S,N} = V \qquad \left.\frac{\partial H}{\partial N}\right)_{S,P} = \mu}$$

Then we have U minus PV we sorry, U plus PV which was the enthalpy and we said that this is a function of S, P and N. So, if this is a function of S, P, N then we said that this is going to be del H del S; P and N are held constant dS del H del P S and N are held constant dP plus del H del N, S and P are held constant dN.

If I look at the right hand side dH is also identical to dU plus P dV plus V dP. dU plus P dV is what? Is T dS plus mu dN. So, that I have V. So, I have T dS plus V dP plus mu dN, right and therefore, immediately the derivatives again follow del H del S, P and N are constant is equal to T del H del P, S and N are constant is equal to V and del H del N, S and P are held constant is equal to the chemical potential mu. One can again reconstruct back the U from these relations.

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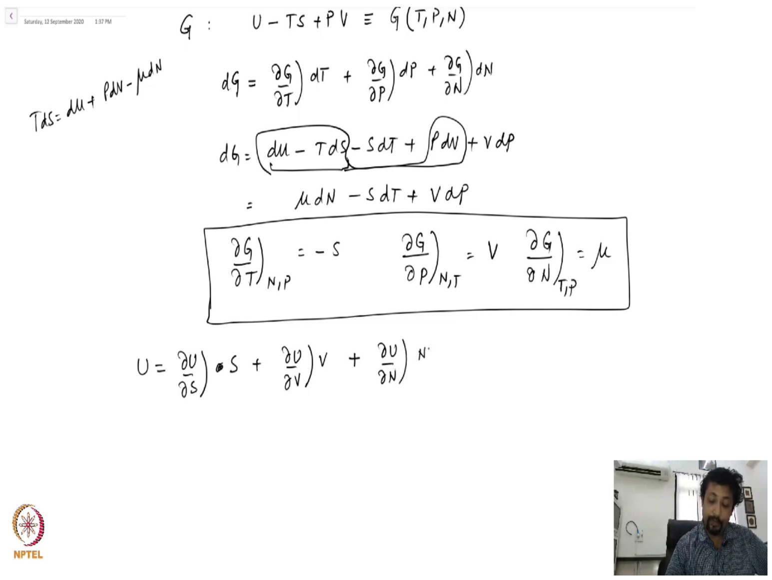

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$$G : \quad U - TS + PV \equiv G(T, P, N)$$

$$TdS = dU + PdV - \mu dN$$

$$dG = \left.\frac{\partial G}{\partial T}\right) dT + \left.\frac{\partial G}{\partial P}\right) dP + \left.\frac{\partial G}{\partial N}\right) dN$$

$$dG = \boxed{dU - TdS} - SdT + \boxed{PdV} + VdP$$

$$= \mu dN - SdT + VdP$$

$$\boxed{\left.\frac{\partial G}{\partial T}\right)_{N,P} = -S \qquad \left.\frac{\partial G}{\partial P}\right)_{N,T} = V \qquad \left.\frac{\partial G}{\partial N}\right)_{T,P} = \mu}$$

$$U = \left.\frac{\partial U}{\partial S}\right) S + \left.\frac{\partial U}{\partial V}\right) V + \left.\frac{\partial U}{\partial N}\right) N$$

What about the third term of interest which is G? G we constructed by replacing both the entropy as well as the volume, so that this was G which was a function of T, P and N. And, if I do it dU sorry, dG is del G del T dT, I am not going to write what is being held constant because now I know that you have a grasp of what is what should be held constant dP plus del G del N dN, right.

So, then dG is also dU minus T dS minus S dT plus P dV plus V dP. So, T dS is dU plus P dV minus mu dN. So, this quantity becomes mu dN minus together with this one. dU plus P dV this becomes minus S dT plus V dP, so that del G del T, N and P held constant is the entropy, del G del P, N and T held constant is the volume and del G del N T and P are held constant is the chemical potential these are the derivatives which are of interest over here.

But, remember we did the Euler relation for the energy. What does that Euler relation give us that U was a function of S, V, N. Therefore, we had del U del S times S plus del U del V times volume plus del U del N times N, right. This was the Euler relation.

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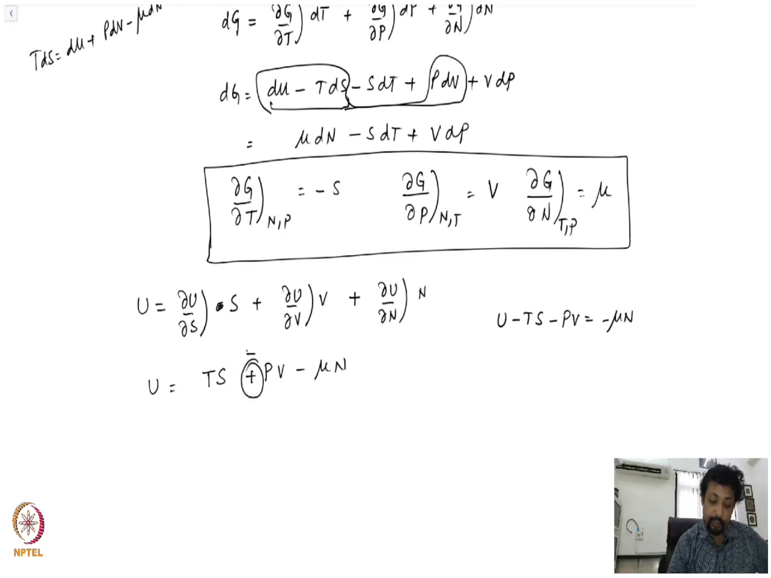

$TdS = dU + PdV - \mu dN$

$$dG = \left.\frac{\partial G}{\partial T}\right) dT + \left.\frac{\partial G}{\partial P}\right) dP + \left.\frac{\partial G}{\partial N}\right) dN$$

$$dG = dU - TdS - SdT + PdV + VdP$$

$$= \mu dN - SdT + VdP$$

$$\boxed{\left.\frac{\partial G}{\partial T}\right)_{N,P} = -S \qquad \left.\frac{\partial G}{\partial P}\right)_{N,T} = V \qquad \left.\frac{\partial G}{\partial N}\right)_{T,P} = \mu}$$

$$U = \left.\frac{\partial U}{\partial S}\right) S + \left.\frac{\partial U}{\partial V}\right) V + \left.\frac{\partial U}{\partial N}\right) N$$

$$U - TS - PV = -\mu N$$

$$U = TS \overset{-}{\textcircled{+}} PV - \mu N$$

So, we knew that U is equal to TS and then this is going to be del U del V is going to be plus PV minus mu N. So, it follows that U minus TS minus PV is minus mu N. There is a problem with the sign over here this has to be minus.

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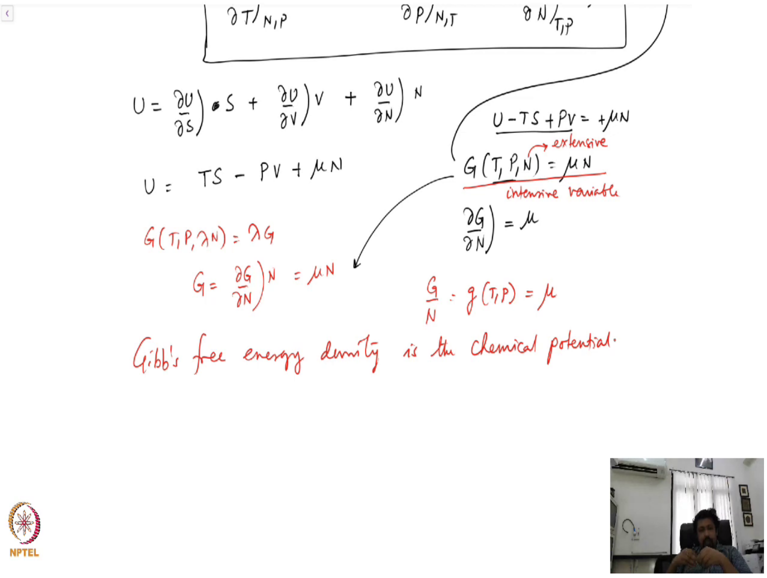

$\partial T)_{N,P}$ $\partial P)_{N,T}$ $\partial N)_{T,P}$

$$U = \frac{\partial U}{\partial S}\Big) S + \frac{\partial U}{\partial V}\Big) V + \frac{\partial U}{\partial N}\Big) N$$

$$U = TS - PV + \mu N$$

$$\underline{U - TS + PV = +\mu N}$$

$$\underline{G(T, P, \overset{\text{extensive}}{N}) = \mu N}$$

intensive variable

$$\frac{\partial G}{\partial N}\Big) = \mu$$

$$G(T, P, \lambda N) = \lambda G$$

$$G = \frac{\partial G}{\partial N}\Big) N = \mu N$$

$$\frac{G}{N} = g(T, P) = \mu$$

Gibb's free energy density is the chemical potential.

So, let us rub this; this has to be minus. So, U minus TS and this has to be plus. U minus TS plus P U is plus mu N. If that is the case then I clearly see that G of T, P, N and this follows all the way from this relation that we have defined is equal to mu times N, correct? So, that del G del N is equal to mu, it is consistent with this definition.

But, what is also consistent is that if you see over here both of these are your intensive variable and there is no homogeneous homogeneity property associated with this. The only thing that is associated with this is N. This is my only extensive variable and therefore, I must have G of T, P lambda N must be equal to lambda times G and if I want to apply the Euler relation I am going to get the same thing as this that N times.

If I want to apply the Euler relation, then this is going to be del G del N times N and this is equal to mu times N which is the relation that I have over here. So, everything becomes consistent with this. Interestingly you should know that once I have this then G by N is small g which is a function of T and P because N has been taken out over here because you have put lambda is equal to 1 by N and that essentially is the chemical potential.

So, the Gibbs free energy density is the chemical potential right. So, that means, it is interesting; that means, how do you define the Gibbs for chemical potential? Well, it is amount of energy the change in the free energy or amount of energy that I have to well, the change in the Gibbs free energy per particle that essentially defines my chemical potential mu.